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FURTHER STUDIES ON CANADIAN LARD: PHOSPHORUS CONTENT, COLOR, AND STABILITY¹

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Abstract

A modified colorimetric procedure showed that phosphorus content of Canadian lard (12 dry rendered samples and 21 wet rendered samples) was generally less than 0.001%, and did not appear to be definitely related to method of rendering or to keeping quality. Color of lard was conveniently measured with the Evelyn photoelectric colorimeter; photoelectric transmission values were most closely related to Lovibond color values in the yellow region. Lovibond color could be predicted only approximately from transmission. No association of color with processing conditions or with keeping quality was found. The criterion of an indicator change by volatile fatty acids in the Swift stability test rather than the attainment of an arbitrary peroxide value by the fat gave a closer association of Swift stability test values with organoleptic storage life of lard.

Introduction

As Canadian lard is resuming its prewar status of a surplus product, further investigations which might lead to the improvement of its stability and general quality have been undertaken. Prior studies dealt with methods for assessing rancidity (7), and with a survey of the major chemical and physical properties of Canadian lard (14). Three leads suggested by these investigations have now been followed up. They deal with measurement of phosphorus content and color of lard and the possible association of these properties with keeping quality and other characteristics; and with certain relations between various measurements of keeping quality. Although the three investigations are not closely related, they are reported in one paper largely because they employed a single set of samples. These samples are briefly described in the next section, and this is followed by three sections dealing with the individual investigations.

Materials

The materials used in this study were characterized in a previous investigation (14). They consisted of 33 samples of lard from 26 packing plants across Canada. Of these samples, 12 were dry rendered and 21 wet rendered.

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Data for Lovibond yellow and red colors ($5\frac{1}{4}$ in. cell, arbitrary units), storage life (weeks at 26.7° C.) by odor tests, Swift stability (minutes at 97.8° C., using both peroxide oxygen and acid-base indicator end points), and processing conditions (confidential) were already available (14).

Phosphorus Content of Lard

The importance of the natural phosphatides in fats and oils as surface active agents, antioxidants, and crystallization inhibitors is well known (3). As information on the amount of phosphatide in Canadian lard was lacking it was considered of interest to examine the available samples in this regard by determining their phosphorus content.

Method

Although the determination of phosphorus has been extensively investigated (11, 24, 25), only a few methods have been developed specifically for glyceride fats and oils (6, 12, 18), in which phosphorus is found chiefly as the orthophosphoric acid of phosphatides. A combination and modification of existing procedures was found satisfactory for rapid analysis of the minor amounts of phosphorus in lard. The molybdenum blue color reaction (5) was employed. The quantity of interfering substances (11, 24, 25) is negligible in materials of the type examined, so no correction for these was necessary. The amounts of the reagents used were critical, as this reaction takes place only in a slightly acid pH range (5). The blue color was stabilized by means of a sodium succinate buffer (22), no change in color density being found up to two hours after the addition of this reagent to test solutions.

Of a number of reagents added to the fat to hold the phosphorus during ignition, zinc oxide proved to be most convenient. The magnesium and calcium oxides available were found to contribute silica, which interferes in the colorimetric reaction (11). With magnesium acetate and magnesium nitrate, satisfactory recovery of added phosphorus could be obtained, but spattering occurred during ignition. With zinc oxide, recovery of added orthophosphoric acid, in the presence or absence of fatty material, was 97% to 100% for ignition at either 500° or 600° C. for one hour in platinum crucibles. The 600° C. temperature was chosen because it resulted in less carbonaceous material in the ash. Phosphorus could be detected to 0.0001%, and duplicate analyses differed by less than 0.0004% phosphorus. The necessary difference for statistical significance (5% level) between average values for different samples was 0.0004% phosphorus.

The efficacy of zinc oxide is said to be due in part to its transformation to the peroxide form at higher temperatures (6). Peroxides may attack platinum, and harm to the metal may also result by alloying if reduction of the zinc compounds occurs, but, under the conditions of this study, it was stated that there is little risk of deterioration of the crucibles.* This was confirmed

*Private communication from Johnson, Matthey & Mallory Ltd., Montreal.

by observation, since the platinum crucibles used did not appear to be damaged after several dozen determinations. Porcelain and nickel crucibles could not be successfully used, as silica and nickel were removed from the crucibles and interfered with the colorimetric reaction.

Details of the phosphorus procedure are as follows:

Reagents

Ammonium molybdate solution, 2.5 gm. of ammonium molybdate per 100 ml. of 0.6*N* sulphuric acid.

Hydroquinone solution, 0.5 gm. of hydroquinone per 100 ml. of water made slightly acid with one drop of concentrated sulphuric acid.

Sodium succinate solution, 20 gm. of sodium succinate (anhydrous basis) per 100 ml. of water.

Zinc oxide powder, reagent grade.

Extracting solution, 0.6*N* sulphuric acid.

Standard solution, 0.4394 gm. of potassium dihydrogen phosphate plus 20 gm. of zinc oxide, made up to 1000 ml. with 0.6*N* sulphuric acid.

Diluting solution, 2 gm. of zinc oxide made up to 100 ml. with 0.6*N* sulphuric acid.

Procedure

(To be done in duplicate.) Weigh 1 gm. (± 0.0002 gm.) of fat or oil carefully into the bottom of a 30 ml. platinum crucible, and cover completely with 2 gm. (± 0.05 gm.) of zinc oxide. Ignite in muffle furnace for one hour at 600° C., maintaining free circulation of air. Extract ash thoroughly with 0.6*N* sulphuric acid, boiling gently for five minutes to change pyrophosphates to orthophosphates, and filter extract through Whatman No. 40 paper into 100 ml. volumetric flask. Make to volume with 0.6*N* sulphuric acid and mix.

Pipette 5 ml. aliquot into colorimeter tube, and add 2 ml. molybdate solution, 1 ml. hydroquinone solution, and 2 ml. succinate solution, *in that order*, shaking between each addition. Do not delay the addition of succinate beyond five minutes. Read in the Evelyn photoelectric colorimeter, using 690 $m\mu$ filter, and setting galvanometer to 100 with water. Obtain amount of phosphorus from calibration curve prepared using the standard solution and diluting solution. Subtract value obtained for blank determination on reagents only.

Results

As shown in Table I, 23 lard samples contained less than 0.0001% phosphorus, eight contained 0.0001 to 0.001%, one contained 0.0014%, and one 0.0053%. The large number of nil values (i.e., less than 0.0001%) precluded

statistical comparison of phosphorus content with other lard data. The phosphorus content of these lards did not appear to be definitely related to their keeping quality (also presented in Table I), or to the method of rendering. The average storage life of samples containing 0.0001% or more

TABLE I
PHOSPHORUS CONTENT AND STORAGE LIFE OF 33 SAMPLES OF CANADIAN LARD

Sample No. **	Phosphorus content, %	Storage life, weeks at 26.7° C.	Sample No. **	Phosphorus content, %	Storage life, weeks at 26.7° C.
1*	0.0053	19.0	18	<0.0001	9.0
2*	0.0014	2.2	19*	<0.0001	8.7
3	0.0007	10.0	20	<0.0001	8.5
4*	0.0007	8.0	21*	<0.0001	7.3
5*	0.0006	6.6	22	<0.0001	7.2
6*	0.0005	15.0	23	<0.0001	7.2
7	0.0004	13.0	24*	<0.0001	6.8
8	0.0003	10.2	25	<0.0001	6.6
9	0.0002	13.8	26	<0.0001	6.6
10	0.0001	8.3	27	<0.0001	6.4
11	<0.0001	23.0	28*	<0.0001	6.0
12	<0.0001	18.0	29	<0.0001	6.0
13*	<0.0001	14.2	30	<0.0001	5.6
14*	<0.0001	12.8	31*	<0.0001	5.0
15	<0.0001	11.4	32	<0.0001	2.8
16	<0.0001	10.0	33	<0.0001	2.6
17	<0.0001	9.8			

*Dry rendered samples.

**Sample No. is given to enable cross reference to Table III.

phosphorus (10.6 weeks) was slightly higher than that for samples containing less than 0.0001% phosphorus (8.8 weeks). The phosphorus content of the dry rendered samples seemed to be generally higher than that of the wet rendered samples.

The phosphatide content of lard is quoted as "up to 0.05%" (3, p. 25), corresponding to an amount of phosphorus of about 0.002%, higher than 32 of the 33 values found in this study. The single high value obtained may be attributable to lecithin added as a stabilizer, although all samples were supposed to be free of added antioxidants. If lecithin was added to this sample (No. 1), it may have had some effect, although sample No. 11, containing less than 0.0001% phosphorus, had a longer storage life.

Since lard is deficient in natural antioxidants (3, p. 222), keeping quality may be influenced more by changes in processing conditions than by variation in the minor amounts of stabilizers present. The apparent lack of association of storage life with phosphorus content may be attributable to the relative ineffectiveness of phosphatides as stabilizers for lard in the absence of tocopherols or other antioxidants of the phenolic type (3, p. 225). Tocopherols are present in lard only in very small amounts (16, p. 18). However, unless the relation of keeping quality to phosphorus content was marked, it could not be demonstrated in the presence of such small amounts of phosphorus.

An earlier investigation indicated that increased amounts of bones in the rendering stock might be responsible for longer storage life in some samples of wet rendered lard (14). It was suggested that lecithin, which is reportedly present in larger amounts in pig bone fat than in lard (10), gave this increased stability. This possible explanation was not supported by the present study, since phosphorus content of lard and amount of bones in the rendering stock did not appear to be related.

The phosphatide concentration was probably too low in all but one or two of the lards examined to exert any surface active or crystallization inhibiting effects (3, pp. 364, 648).

Color of Lard

The relation of lard color to processing conditions and to stability was examined, and in view of the continuing scarcity of Lovibond color glasses (2, 23), an attempt was made to relate Lovibond color of lard to photoelectric transmission at various wave lengths.

Measurements of light transmission were made with the Evelyn photoelectric colorimeter on filtered samples held at 60° C., using light mineral oil (Stanolax) to set the galvanometer to 100% transmission. Average light transmissions by the Evelyn photoelectric colorimeter for all lards at different wave lengths are shown in Table II. Table III presents transmissions at 440 and 520 m μ compared to Lovibond yellow and red colors respectively. Prediction equations for color measurements made according to the Lovibond and Evelyn systems, standard errors of estimate, and correlation coefficients are given in Table IV.

There was no significant difference between the color of wet and dry rendered lards by either Lovibond or photoelectric measurements. Dry rendering did not yield more highly colored lard than wet rendering, in spite of the higher processing temperatures involved in the former method. Presumably the coloring substances in the dry rendered stock were not dehydrated so seriously as to enter the lard in any appreciable amount (3, p. 461). Color was not statistically related to storage life or to processing factors (amounts of killing fat, cutting fat, bones, and sweet pickle material in the rendering stock; rendering time and temperature; filtering temperature; and time between processing and packaging) for wet and dry rendered lards considered together or separately.

The relation between light transmissions and the corresponding Lovibond colors was closer for yellow than for red. The error of estimate was high in every case, as the average Lovibond color was 8.6Y, 1.6R. The highest correlations were found for Lovibond yellow and Evelyn 440m μ , and for Lovibond red and Evelyn 520 m μ ; but the prediction of Lovibond values from these Evelyn transmissions would be only approximate, in view of the large errors of estimate. The possible prediction of Lovibond color values

TABLE II
AVERAGE LIGHT TRANSMISSION (EVELYN COLORIMETER) OF 33 SAMPLES
OF CANADIAN LARD
(Relative to mineral oil)

Wave length, $m\mu$	Transmission, %	Wave length, $m\mu$	Transmission, %
420	69	565	96
440	78	580	97
470	83	620	98
490	91	635	99
520	94	660	99
540	95	690	100

TABLE III
COMPARISON OF LOVIBOND COLOR READINGS AND EVELYN PHOTOELECTRIC TRANSMISSION
VALUES FOR 33 SAMPLES OF CANADIAN LARD

Sample No.**	Lovibond yellow color, arbitrary units, in decreasing order of magnitude	Evelyn photoelectric transmission % at 440 $m\mu$, relative to mineral oil	Sample No.**	Lovibond red color, arbitrary units, in decreasing order of magnitude	Evelyn photoelectric transmission % at 520 $m\mu$, relative to mineral oil
14*	22.3	60	14*	3.1	85
2*	19.5	57	18	3.1	88
21*	19.5	66	12	3.0	92
5*	14.0	68	21*	2.8	90
33	13.4	75	32	2.7	95
12	12.3	75	2*	2.4	86
18	11.6	70	7	2.1	94
6*	11.3	70	20	2.0	89
32	11.2	78	5*	2.0	90
8	11.0	75	15	2.0	90
30	10.0	77	33	1.9	93
9	9.2	80	8	1.9	93
26	8.3	74	26	1.8	92
11	8.1	81	30	1.7	94
17	8.0	75	6*	1.7	91
7	7.9	81	17	1.4	93
20	7.7	80	22	1.4	95
22	7.7	80	1*	1.2	94
1*	7.3	74	11	1.1	94
15	7.0	77	27	1.1	95
28*	6.4	86	29	1.0	97
24*	6.1	82	3	1.0	95
4*	5.8	84	16	1.0	96
3	5.1	82	24*	1.0	95
27	5.1	82	28*	1.0	97
13*	4.3	85	9	1.0	96
19*	4.3	90	23	0.9	97
16	3.4	87	10	0.9	97
10	3.4	86	19*	0.9	100
31*	3.4	86	25	0.8	97
23	3.3	87	4*	0.8	97
29	3.3	87	13*	0.7	98
25	3.0	85	31*	0.4	98

*Dry rendered samples.

**Sample No. is given to enable cross reference to Table I.

from photoelectric transmission has been suggested by others, and since the inception of this work the use of spectrophotometry as a standard method for measuring the color of fats and oils (without reference to Lovibond equivalents) has been recommended (1).

TABLE IV
STATISTICAL RELATIONS BETWEEN LOVIBOND AND EVELYN COLOR
MEASUREMENTS ON 33 SAMPLES OF CANADIAN LARD

Quantities correlated	Correlation coefficient	Prediction equation	Standard error of estimate
Lovibond yellow (y) and Evelyn* 420 m μ (x)	-.90	$y = -.461x + 40.4$	± 2.2
Lovibond yellow (y) and Evelyn 440 m μ (x)	-.93	$y = -.579x + 53.9$	± 1.9
Lovibond yellow (y) and Evelyn 470 m μ (x)	-.90	$y = -.661x + 63.9$	± 2.2
Lovibond red (y) and Evelyn 470 m μ (x)	-.77	$y = -.086x + 8.7$	$\pm .5$
Lovibond red (y) and Evelyn 490 m μ (x)	-.80	$y = -.134x + 13.8$	$\pm .5$
Lovibond red (y) and Evelyn 520 m μ (x)	-.82	$y = -.180x + 18.5$	$\pm .4$
Lovibond red (y) and Evelyn 540 m μ (x)	-.79	$y = -.233x + 23.8$	$\pm .5$

*Evelyn color measurements are expressed as percent transmission relative to mineral oil.

As colorimeter readings for most of the samples approached 100% transmission relative to mineral oil at wave lengths of 540 m μ or over (Table II), associations of Lovibond colors with transmissions at wave lengths over 540 m μ were not examined. Occasional lard samples may show a blue shade; the amount of blue color could be estimated with the Evelyn colorimeter at 660 m μ .

Stability of Lard

The association of organoleptic and chemical estimates of keeping quality of lard was given further study, as this has been the subject of some question (14, 20). This section deals only with further statistical studies of earlier data (14) on lard stability determined organoleptically for lard stored at 26.7° C., and determined by the Swift accelerated aeration test at 97.8° C. In the Swift stability test the end of the induction period was estimated by determining peroxide oxygen values on the heated and aerated lard, and also by passing the air leaving the aspirated lard into an indicator solution (brom-cresol green) sensitive to the volatile fatty acids produced during the oxidative deterioration of the lard (15).

The regression equations relating the various methods for determining storage life are shown in Table V, together with standard errors of estimate and correlation coefficients. Organoleptic storage life at 26.7° C. was more closely correlated with Swift stability by the indicator end point method

than with Swift stability by the peroxide end point method, although the two estimates of Swift stability were closely associated. Errors of estimate were high, enabling only approximate prediction. Swift stability of 100¹min.

TABLE V
STATISTICAL RELATIONS BETWEEN ORGANOLEPTIC AND CHEMICAL MEASUREMENTS
OF STABILITY ON 33 SAMPLES OF CANADIAN LARD

Quantities correlated	Correlation coefficient	Prediction equation	Standard error of estimate
Log storage life by odor panel* (y) and Swift stability ** by indicator end point (x)	.83	$y = .0012x + .66$	$\pm .14$
Log storage life by odor panel (y) and Swift stability by peroxide oxygen end point (x)	.72	$y = .0011x + .75$	$\pm .16$
Swift stability by peroxide oxygen end point (y) and Swift stability by indicator end point (x)	.96	$y = .9000x - .49$	$\pm .44$

*Weeks at 26.7° C.

**Minutes at 97.8° C.

by indicator corresponded to about 40 min. Swift stability by peroxide; and to about six weeks storage life at 26.7° C. by organoleptic estimate. Further details of the association of these tests are shown in Figs. 1 and 2.

The use of the indicator end point method for determining Swift stability appeared to be convenient, as suggested in earlier reports (13, 15). The greater values obtained for Swift stability by the indicator method as compared with those obtained by the peroxide method were presumably due to the period taken for sufficient fatty acid material to be distilled from the fat into the indicator solution. This time lag could be arbitrarily shortened by carrying the indicator change to a less pronounced stage. However, it would appear preferable to wait for a definite indicator change, since the breakdown of peroxides to acidic and other products is usually greatly accelerated in lard after the peroxide value has reached about 10 ml. of 0.002*N* thiosulphate per gm. (the peroxide end point of rancidity).

The rancid odor and flavor of oxidized fats are generally considered due to aldehydes of medium molecular weight, particularly heptylic aldehyde and, to a lesser extent, nonoic aldehyde (19). However, solutions of heptylic aldehyde in mineral oil and in fresh cottonseed oil, although suggestive of rancidity, do not reproduce the typical smell of an oxidized fat (4). The odor of a mixture of lower fatty acids obtained as a by-product in a permanganate oxidation of glycerides more closely resembles that of a highly rancid fat than does heptylic aldehyde (8). Moreover, the aldehydes formed are transitory in nature and the aldehyde content of autoxidizing, purified fatty acid substrates is never great; once formed, aldehydes are quickly oxidized

by the peroxides or other autooxidation products to acids, or they spontaneously decompose to acids (17).

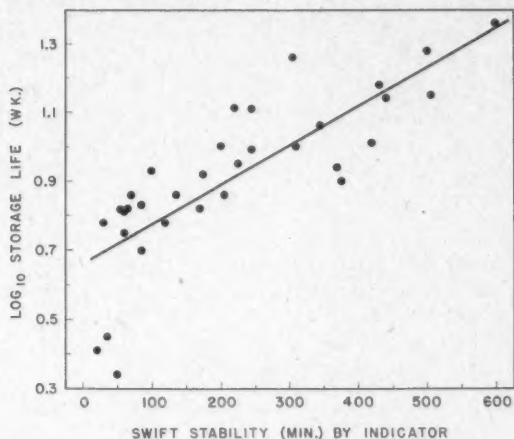


FIG. 1. Relation of Swift stability of lard at 97.8° C. by indicator end point to storage life of lard at 26.7° C. by organoleptic estimate.

In view of these statements it may be assumed that volatile fatty acids are at least partly responsible for the odor of rancidity. Thus the use of an acid-base indicator in the Swift stability test appears to be a rational aid

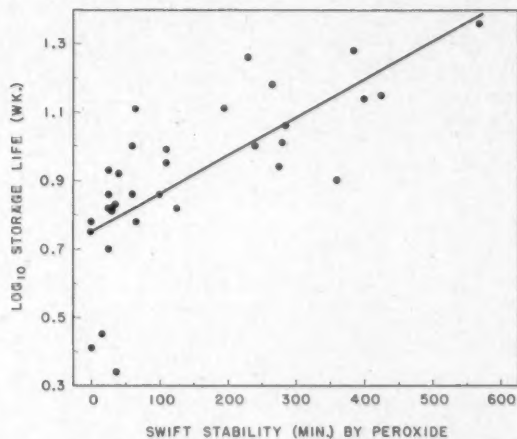


FIG. 2. Relation of Swift stability of lard at 97.8° C. by peroxide oxygen end point to storage life of lard at 26.7° C. by organoleptic estimate.

to the usefulness of this method (9, 21). The objection might be raised that much volatile fatty acid formed by enzymic or bacterial action may be present in an otherwise nonrancid fat, but this drawback would not generally apply

to freshly processed lards and shortenings. The indicator may be renewed after the volatile free fatty acids originally present have been driven off (14). In view of the instability of the aldehydes, the free fatty acids formed from the aldehydes (or arising independently as a result of peroxide breakdown) should constitute a better means of estimating the end of the induction period than the aldehydes themselves. Furthermore, the fat peroxides formed in different fats vary in stability (3, p. 43). The indicator end point should therefore be a better criterion of the end of the induction period than an arbitrary peroxide value.

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STRESS-STRAIN CURVES FOR FATIGUED RUBBER¹

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Abstract

It is shown that with natural rubber, vulcanized to soft "gum" rings, extension curves after the first are in two parts, and that the second part does not develop except after severe previous extensions.

With molded rings, stretched initially a few per cent short of rupture, these effects are very marked, and the fifth extension curve is in two clearly separate parts with a sharp inflection at 380% elongation. The equations fitting both parts of this curve are of the form:

$$F/A = K_0L + K_1L^4 - K_2.$$

In these equations, the two K_0L terms intersect at $L = 0$, and the equations also show a number of other coincidences which strongly suggest that they must be of significance as related to the elasticity of rubber after fatigue has produced a stabilized structure.

It is also shown that with these fatigued rings no hysteresis occurs within the range from 0 to 110% elongation, irrespective of the range of the elongation and retraction cycle; that extensions within the range from 0 to 380% elongation show no hysteresis on retraction; but that hysteresis commences abruptly if 380% elongation is exceeded.

Hysteresis effects for a "small loop" also differ markedly, depending on whether the loop is initiated from an elongation or retraction curve, and continued cycling round this "small loop" does not remove this difference.

Since the equations for both parts of these extension curves are of exactly identical form, although hysteresis occurs in one part but not in the other, it is suggested that the basic cause of elasticity of rubber cannot be considered as in any way related to any molecular arrangement factors, but must be of a kinetic nature, and it is shown that if it is assumed that the rubber chain is vibrating, and that tension in the chain restricts this vibration, the forces developed would be quite adequate to explain the elasticity.

It is also shown that with fatigued rubber the S shape of the extension curves is entirely destroyed if forces are calculated on the basis of force per unit area under stress, while this is only approximately the case for the usual extension curves.

It is suggested that if the extension curve for rubber, and possibly other substances, is extended back to $L = 0$, it should give an intercept equal to the internal pressure in the substance, i.e., that Young's modulus represents the internal pressure of the substance.

In attempts to evaluate the fatigue properties of a number of supposedly uniform rubber rings, it was found that although all rings gave a very closely uniform extension curve the first time they were stretched, if they were stretched a second and third time, the terminal portion of their extension curves from about 400% elongation showed very marked variations between different rings, although below 400% agreement was quite good.

Attempts to secure more uniform fatigued rings were not very successful until it was noted that the deviation in the terminal portions of the curves was closely related to very small differences in the amount by which each ring had been stretched in the first extension; as this initial extension was increased, the tip of the second and third extension curves bent more sharply upwards (towards greater extension, or less force).

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These rubber rings were standard Schopper cut rings, but despite care in cutting, the cross sections showed appreciable variations, and, as the effect under consideration appeared to be related only to the final 40 or 50% of elongation, special ring molds (9) were used in order to reduce dimensional variations to a minimum.

Since these molded rings were free from surface scratches and of much more exact dimensions, they allowed considerably more extension, and as they were also free from thin spots, statistical variations in stress at break were reduced by a factor of about 5. For this purpose, these rings, therefore, were a tremendous improvement, since the higher elongations were also combined with a much greater safety factor, and fewer rings were therefore lost by premature breaking.

With these rings, the effects of fatigue on the locus of the breaking point was determined by breaking one ring on the first elongation, then a second ring was taken just short of this elongation (6 or 8 mm. on the Schopper curve) returned to zero and broken on the second elongation, a third ring then being taken just short of breaking on a first and second stretch, and broken on the third, etc. The area within the locus of these breaks, therefore, defined the forces and elongations which could be applied safely during a fatigue test without much risk of premature failure of the ring. These extensions were all taken at half the usual rate, or at 10 in. per min., in order to obtain smoother curves than could be obtained at 20 in. per min.

Curves taken with these rings at once showed that the previous irregularities were due to the fact that after severe initial extension a stress-strain curve of fatigued rubber is not continuous, but is actually in two parts, with an almost abrupt inflection between them. Comparison with the results on cut rings showed that this effect developed only partially with lesser extensions, and consequently did not give stable results near the tip of the extension curves for fatigued cut rings.

Techniques for the Best Development of This Effect

Two general methods can be used to obtain the best development of these double extension curves: (a) continually increase the elongation within the safe locus as a ring is repeatedly stretched; or (b) stretch a ring once only very close indeed to its ultimate elongation, and on repeated stretches take it again to this same elongation.

With method (a) the ring rapidly becomes weaker, but permits enormous elongation; this method, in effect, develops a long second part of the extension curve, but greatly at the expense of strength; there is also the risk of developing fatigue cracks which destroy the value of the curves as the cross section becomes unknown. Method (b) however, does not weaken the ring as much but does serve to sharpen up the transition between the two parts of the curve, and, although the second part of the curve is naturally shorter, with careful measurement it is quite adequate for exact characterization.

It was expected that rings stretched repeatedly to a certain elongation might show anomalies if later taken past this value. This is not the case, however, since if rings are "developed" by both methods (a) and (b) above until the lower parts of their extension curves agree, and are then taken to their points of failure, it is found that the upper parts of their curves also agree. Apparently, when a ring is extended past the inflection point, a relatively regular arrangement of the rubber chains is produced and it therefore makes little, if any, difference how this regularity is initially produced.

It is noticeable, however, that the sharpest inflection point is produced by repeated stretching to the same elongation, probably because it requires a greater number of cycles to obtain the same degree of "development". This method was therefore used for all curves to be examined in detail.

Fatigued Stress-Strain Curves

Fig. 1 gives a reproduction of a family of five consecutive tests on one ring, taken without rest between each test. It will be seen that the kink in each elongation curve becomes sharper with each stretch, and, that for a

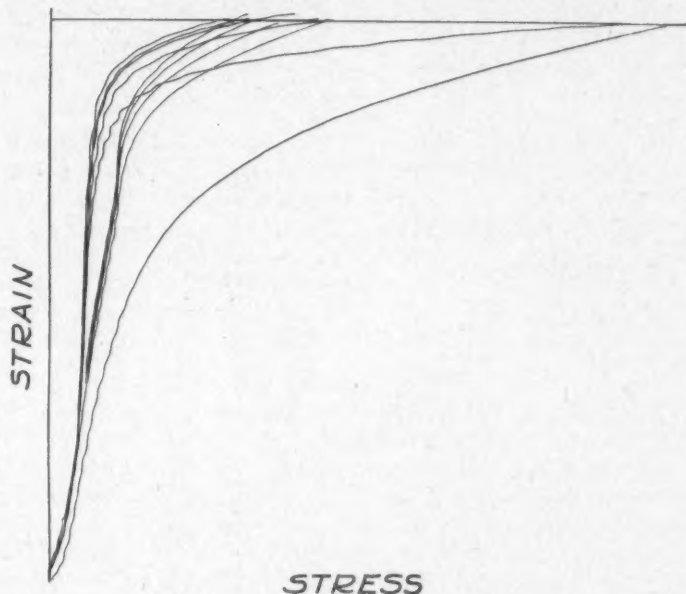


FIG. 1. Successive elongation cycles of "gum rubber" rings.

short distance beyond the kink, the curve becomes almost vertical with the third, fourth, and fifth test. (The waves on these curves are due to the difficulty of preventing oscillations of the pendulum, although the toggles were lifted and a second operator caught the pendulum if the ring failed.)

After the first, each of these extension curves is clearly a composite of two parts, and this separation is very fully developed with the fifth extension. All subsequent discussion relates to this fifth extension curve of rings of this same mix, treated in exactly the same manner as shown in Fig. 1.

Rubber Recipe

The composition used was:

Smoked sheet	100.0 gm.
Sulphur	3.0 gm.
Stearic acid	1.0 gm.
Zinc oxide	2.5 gm.
Captax	0.4 gm.
V.G.B. (antioxidant)	0.5 gm.

and rings were cured 67 min. at 133° C., cure being initiated and arrested very quickly by immersion of the hollow ring molds in a large well stirred paraffin wax bath and in cold water respectively.

This stock has only a minimum of vulcanizing agents and cured to a very clear "gum rubber" with very little opacity; its physical properties therefore should closely approximate those of rubber substance, unaffected by any properties of "fillers".

The rings were 44.5 mm. inside diameter, 3.15 mm. thick, and were always made 6 or 7 mm. wide in order to prevent the rings turning over or on edge when under test. Twenty-four hours were also allowed between curing and test in order to allow the rubber to "settle down".

Hysteresis Phenomena with Fatigued Rings

Fig. 2 gives a graph of a fifth stretch, and the various parts of the curve are marked for convenient discussion, curve *OAB* showing the complete extension curve (5th cycle) and *BCDO* showing the complete retraction curve.

If the hysteresis loop is completed, line *CD* reaching line *OA*, the complete cycle can be repeated, the only effect being slight further "development" of the ring with each cycle, giving slightly greater extensions and lower forces. It is not therefore necessary to pass back to *O* in order to repeat the cycle, and part *OD* of the curve is absolutely reversible, without regard to the history or extent of the stretch and retraction cycle.

The junction of *CD* with *OA* appears quite abrupt, but if an original record, e.g., such as the original of Fig. 1, made with a very fine pen, is examined, it will be seen that there is an extremely slight merging curve at the end of *CD*. If this return curve *CD* does not quite pass beyond the end of this slight merging curve, and therefore fails actually to reach line *OA*, although its deviation from this line may be barely perceptible (e.g., 0.1 mm. on a standard Schopper record), if the return is interrupted at this point and the

ring stretched again, the main cycle will not repeat, but a hysteresis curve will be produced of a type discussed later in Fig. 3. In other words, the apparent point *D* must be passed on a standard Schopper tester by about

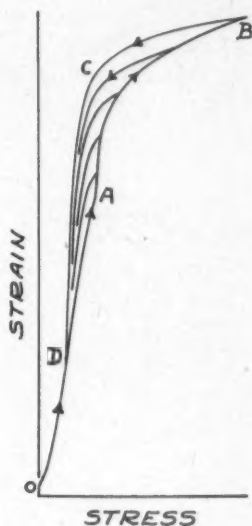


FIG. 2. Fifth cycle and "intermediate return curves".

2 or 3 mm. before the main cycle is again reproduced. No delay, or "slow melting" effect however is shown, as once point *D* is passed by this amount, curve *OA* can be reproduced immediately by continuing the extension again.

Intermediate Hysteresis Effects

With these fatigued rings part *OA* of the curve is free from any detectable hysteresis, and the curve may be traversed in both directions a number of times within these limits with no detectable change in the ring. If the ring is stretched past point *A*, however, retraction shows marked hysteresis and a family of intermediate return curves can be taken as shown within the main loop. These intermediate return curves were taken with the same ring as the main complete cycle, but unless extension *B* is closely approached, further "development" of the ring is very slight, and its extension properties still agree closely with the main curve.

These intermediate return curves clearly emphasize the importance of points *A* and *D* in these extension curves, since hysteresis loops do not develop at all unless extension *A* is exceeded, and the return curves are all directed towards point *D* (instead of crossing the loop and merging with *CD*, as might perhaps be expected).

Intermediate Forward Curves

As shown in Fig. 3, a very different class of result, however, is produced if the fifth stretch and return cycle is taken as before, but is interrupted at some point between *C* and *D*, extension then being taken from this point. In this case, the main loop in the figure was taken with one ring and the intermediate forward curves with another, since the first ring would be "developed" further by the full extension of the cycle and would no longer give results in agreement with its fifth curve.

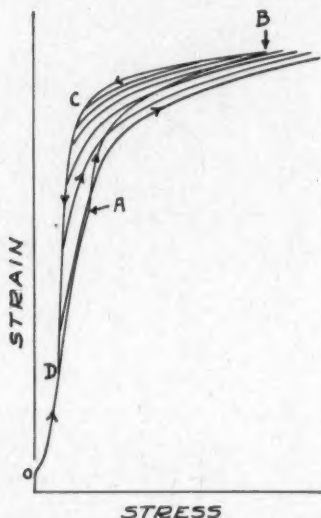


FIG. 3. Fifth cycle and "intermediate forward curves".

These intermediate forward curves are very different from the intermediate return curves of Fig. 2, in that they are not enclosed by the main hysteresis loop but cross line *AB* sharply, i.e., produce stiffer rubber than is available by simple extension.

"Small Loop" Hysteresis Effect

If the stresses in a fatigued ring are constantly maintained so that they are always greater than shown by curve *DA*, but less than by curve *CB*, of Figs. 2 or 3, and a small extension and retraction cycle instituted forming a "small loop", hysteresis effects will be found to differ considerably, depending on whether this small loop is entered from curve *AB* or from *CD*.

If this small loop is taken following an incomplete extension (i.e., the loop is entered from curve *AB* as in Fig. 2) it will be found to show considerable hysteresis, and continued cycling round the loop does not remove this hysteresis.

On the other hand, if the small loop is taken following an incomplete retraction (i.e., the ring is fully extended to *B*, and retraction is interrupted short of *D*, the loop being entered from the curve *CD* as in Fig. 3), it will be found that the loop shows practically no hysteresis, the slight friction in the tester being adequate to prevent any definite conclusion whether indeed any real hysteresis occurs.

The intermediate forward curves of Fig. 3 are therefore essentially reversible, while the intermediate return curves of Fig. 2 are not.

The curves showing these effects in detail are not given, as they do not indicate any very definite phenomena, but it is clear that small scale hysteresis effects differ markedly, depending on whether the maximum extension is only slightly past the critical value *A* or if the specimen has been taken to full extension and returned partially.

Mathematical Examination of a Fifth Stretch Curve

In order to measure this curve as accurately as possible a sheet of glass was waxed and with a ruling machine marked into small squares all over. After etching and blackening the lines, this was placed over the Schopper curves and the whole enlarged photographically to about 50 by 70 cm. On this large print the mean curve through the waves was sketched in and read from the reference lines. By this process, after conversion back to the same size as the original, the dimensions of the original curves can be obtained with considerable precision.

The values obtained were plotted by a very wide variety of methods and tested to see if they would fit almost every probable type of equation. Of all mathematical bases tested, however, only one appeared of any use whatever, and this is so simple and fits the data so exactly that there seems little reason to doubt that the equations, when properly understood, must be of significance.

Equations Developed

It has been known for many years that if an extension curve for rubber is computed as force per actual unit cross section at each instant, and is plotted against the elongation, such curves no longer show the characteristic S shape. As far as the author is aware, however, this method has resulted in no simplification when applied to the mathematical form of initial elongation curves, but it was tested in this case to see if it would yield any useful result.

Calculated in this way, the subtle S shape for the first part of the curve was changed to a perfectly smooth curve in which the slope increased very regularly throughout its length, and the second part of the curve also was of generally similar form. As these curves closely resembled "power curves" of some sort, successive differential curves were prepared by differences between successive measurements, and also by drawing tangents to the curves. These differential curves were then adjusted so that at each stage integration reproduced the parent curve.

The final equations found for the two parts of the fifth extension curves were:

$$\frac{F}{A} = 13.70L + 0.0816L^4 - 13.75, \quad (OA)$$

$$\frac{F}{A} = 22.68L + 10.31 (L - 4.63)^4 - 13.75, \quad (AB)$$

in which F = number of kilograms applied,

A = Actual section, in square centimeters under stress, calculated from original volume of rubber and total length recorded,

L = Total length on the basis of length before fifth extension = 1.0.

It will be observed that there is a slight residual error of 31.6 gm. per sq. cm. in the equation (OA) at $L = 1$. This is due to the fact that this initial reading was also taken from the Schopper record and was not treated in the analysis as having any greater significance than any other reading. These equations, however, fit the entire curve for every individual reading within errors smaller than the thickness of the line in the Schopper record, although a special pen and ink was developed in order to obtain specially precise records. It will be observed, for instance, that in the term $13.70L$, the above error is in the fourth significant figure.

Fig. 4 gives plots of these equations in which curve 1 duplicates the Schopper record of the 5th stretch; curve 2 is the derived form for $F/A : L$, while curves 3 and 4 give the lower parts of curves 1 and 2 respectively, magnified horizontally in order to show their detailed form more clearly. Curves 2 and 4 are extended back to $L = 0$ while curves 1 and 3 naturally stop at $L = 1$.

It is realized that graphs of practically any form may be fitted by complex power series, but these equations are so simple and show so many singular points that it would appear that they can hardly be a casual approximation, but must in some way relate specifically to the process of stretching rubber.

The singularities shown by these equations may be listed:

- (a) Both equations are of identical form.
- (b) Neither equation includes any powers other than first and fourth.
- (c) All terms in the equations contribute major factors, i.e., none are of the nature of small corrections.
- (d) Both equations fit the curves with great accuracy, and the constants can in fact be determined to four significant figures, with residual errors not greater than ± 3 units in the fourth figure.
- (e) The linear part of both equations (if projected back to values of L less than 1.0) intersect at $L = 0$ (giving an intercept of -13.75 kgm. per cm.²).

- (f) The point of origin for the fourth power term of equation (OA) is also at $L = 0$; -13.75 kgm. per cm^2 .
- (g) The point of origin for the fourth power term of equation (AB), while not quite as significant as for equation (OA), is very close to the singular point A, i.e., at $L = 4.63$ while A is at 4.80.

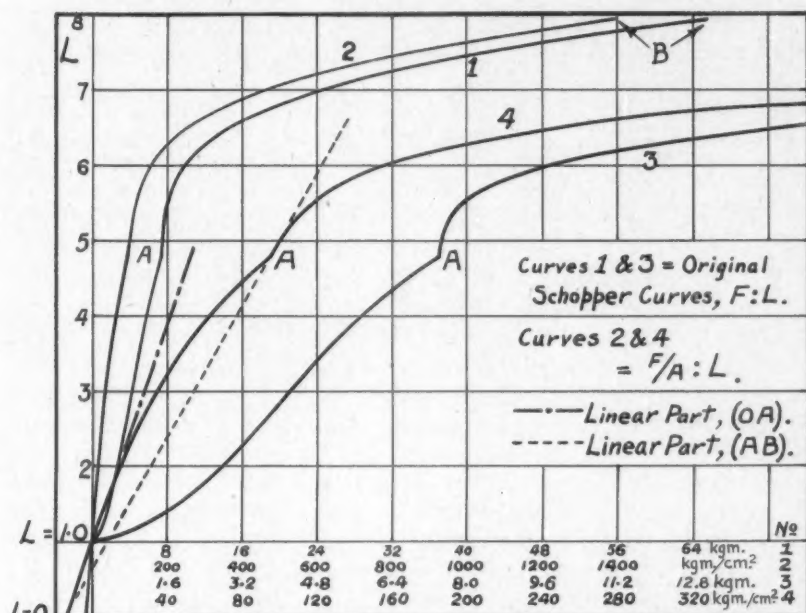


FIG. 4. Plots of 5th stretch curves from equations. (3 and 4, lower parts of curves 1 and 2, magnified horizontally.)

- (h) A very careful examination of the data showed that if the fourth power were altered to 3.98 or 4.02, the linearity of the residue was destroyed, and the amount of deviation from linearity was closely equal in both cases, but opposite in sign. It can be stated from this calculation that to fit these curves the fourth power is correct within about ± 0.005 unit.

Since these equations are so simple and show so many peculiarities, it would appear certain that they must be of significant form with respect to the elastic properties of rubber, since it could not be expected that casual equations would fit the curves so exactly, nor could they reasonably be expected to show so many coincidences.

Discussion of Equations

It will be noted that F/A is in pressure units, and the linear parts of these equations would appear to be analogous to the perfect gas laws, since length-

wise extension of rubber can be considered as identical with sideways compression.

Thus, if V is the volume of rubber per centimeter length of the ring at any instant during an elongation, the length L of the ring is inversely related to V (the small volume changes on extension being neglected).

The equation $\frac{F}{A} = KL$ for the linear portion of the stretching process, considered as a lengthwise extension, can therefore be transformed to the form: $P = \frac{K}{V}$ for the same process, but considered as a sideways compression.

Considered in this way, therefore, extending a fatigued rubber ring should initially follow the gas law until deviations set in, i.e., until the term in L^4 becomes appreciable. The constant term -13.75 kgm. per sq. cm. must therefore be considered as the internal pressure of this rubber in its unstretched condition, as this is the amount by which the first part of the extension curve is developed (from its real origin at $L = 0$) by the time it reached $L = 1$.

The linearity constants in the two equations, 13.70 and 22.68, respectively, evidently represent the gas law compressibilities of the two modifications of rubber. In the range covered by equation OA and where the L^4 term is unimportant (up to about 120% elongation) the molecular arrangement of the rubber must be essentially random, while at the higher elongations covered by equation AB , the rubber is presumably in some more regular arrangement and therefore would be expected to show less compressibility, i.e., its compressibility modulus is the greater.

It is much more difficult, however, to make any suggestion concerning the structural origin of the term in L^4 especially in view of the great range in L over which it applies, and the precision with which its constants can be determined.

General Discussion

It must be assumed that the ring at point O before this 5th extension is in an essentially random molecular arrangement; consequently, since curve OA is reversible, it can only be assumed that either this random molecular arrangement does not change during the reversible part of the extension, or any changes which do occur are of a fluid and reversible nature.

It is suggested, therefore, that during part OA of the curve, both of these assumptions are correct in that relatively short lengths of rubber chain glide over each other in a fluid manner, being assisted by their Brownian movements, but that this process does not involve any changes in the molecular arrangements of the "junction points" between the chains. These junction points presumably include all forms of cross-linkages, hydrocarbon branching, vulcanization points, and chain entanglements, but although during extension

of a ring these junction points become closer together in a section of the ring, and farther apart in the lengthwise direction, it appears necessary to assume that their pattern does not otherwise change since it would seem unavoidable that changes in cross-linkage pattern would involve hysteresis effects on retraction.

Elongation of such a mass of tangled rubber chains could not stress all chains equally, as that would be contrary to the assumption of randomness; consequently, some chains carry high stresses and some low. Fig. 5, *OA*, is intended to illustrate as a two dimensional diagram the type of molecular arrangement which would result, in which thin bars are heavily stressed and thick ones but little.

It is necessary then to consider what occurs at the inflection point *A*.

It might be considered that crystallization starts at point *A* and continues throughout curve *AB*. This, however, is inadequate since such crystallization occurs on stretching all rubber but does not result in an inflection point and furthermore, if such crystallization produces the inflection point, it must be assumed that its continuation would add what would amount to a continuous series of inflections all along the curve. Since, however, the mathematical form of both parts of the curve are identical (and as applied to a "statistical mass" rather unusual) it would appear impossible to assume that crystallization could produce an inflection but as a continuing phenomenon would not affect the mathematical form of the resulting curve.

By the above reasoning it is clear that whatever process produces the inflection, it must in all probability occur all at once and not as a continuing phenomenon. There can, however, be little doubt that crystallization is, in fact, one of the major molecular processes during the whole of curve *AB*, and crystallization therefore cannot be the cause of the inflection point.

In attempting to find the cause of the inflection it must be remembered that this inflection occurs only with rings which have been stretched extraordinarily severely on their initial elongation. Consequently, it would appear that its explanation must be closely related to processes occurring in a severe stretching. It is therefore suggested that the significant process is probably the breaking of all molecular arrangements which cannot accommodate themselves to this stretching. After such a stretch, therefore, the entire specimen would consist of rubber chains of essentially the same length. In other words, if a rubber chain is followed through the length of the rubber (while highly stressed) whichever forward direction one takes at each junction point, all chains will be found to be of the same total length.

It will be seen that, measured over a large number of junction points, this condition is in reality self-contained in the conditions of randomness, but, in rubber which has not been severely stretched, this condition does not apply if the chain length is measured over a small number of junction points.

In the severe stretching of rubber, therefore, the chains need not break but only the junctions between chains, since it is the cross-linkages which prevent the full expression of the uniform fiber length of the rubber chains.

The severely stretched rubber under present discussion, therefore, differs from ordinary rubber in that no cross-linkages are present which would hinder the full extension of all the rubber chains. As the rubber is extended, giving curve AB , by the time B is approached, the entire specimen must therefore closely approach the condition of a compact bundle of parallel rubber chains each containing the same amount of rubber and each carrying the same stress.

Processes at the Inflection Point

From the above reasoning, it is suggested that when the rubber is stretched, giving first the reversible curve OA , as A is approached the accumulation of unequal stresses eventually exceeds the restraining influence of Van der Waal's

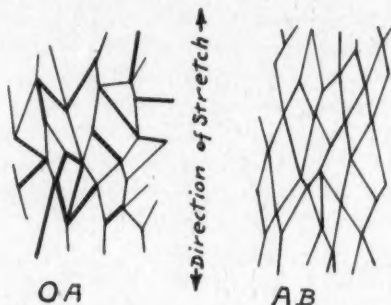


FIG. 5. Diagram of cross linkage modes in fatigued rubber.

(Thick bars are less stressed.)

OA . Unequal "pathways" and stresses.

AB . Equal "pathways" and stresses.

forces, and, at some point within the chain structure, entangled chains suddenly become rearranged in order to redistribute stresses more uniformly.

Since this process would throw unbalanced stresses on neighboring chains, the process becomes cumulative, and the random stresses of Fig. 5, OA , are suddenly replaced by the essentially uniform stresses of Fig. 5, AB . This process, therefore, occurs but once in the extension, and except at the inflection point, has no effect on the elastic processes themselves. The same elastic processes, therefore, are taking place throughout both parts of the curve, with, however, the difference that since the random arrangement, OA , and the organized arrangement, AB , amount to different phases, their elastic constants are naturally different.

It might be enquired why crystallization (which can hardly be operative during, say, the early part of curve OA) has no effect on the mathematical form of curve AB , during which crystallization must be active, but since

crystallization consists merely of the replacement of random Van der Waal's forces by similar forces in organized arrangements, no new force is involved in crystallization. The primary effect of crystallization, therefore, is merely to produce hysteresis on retraction.

There is no doubt a second order effect due to the fact that the forces of crystallization are slightly larger than the random forces they replace. This is shown, for instance, by the volume changes on stretching, but as the present F/A is calculated on the basis of no volume change, this effect is hidden. If, therefore, the actual section of the rubber were determined throughout an elongation, equation AB given above would require correction for these volume changes.

The present equations evidently refer simply to extension tests of a certain number of rubber chains, and include volume changes as part of the process. If equations OA and AB are adjusted for volume changes this would destroy their simplicity, the coincidences between these two equations would not occur, and the resulting equations would be of no value in the present discussion.

Hysteresis

The hysteresis phenomena can be explained readily on this basis if it is also assumed that, when crystallization is produced by extending the ring past the inflection point A , the first parts of the chain to crystallize are not the same locations which prove to be most stable during the "uncrystallization" process, on passing along the curve from C towards D . If this is the case, hysteresis phenomena will obviously differ, depending on whether the "small loop" is approached from curve AB or from CD , since the initial "crystal seeds" differ.

Such assumptions would also explain why the complete extension and retraction cycle cannot be duplicated unless point D is actually passed (on the return from a previous extension beyond A). If even the slightest trace of crystallization remains, as is the case for instance when taking an "intermediate forward" curve, on re-extension, it would be expected that these crystal nuclei would grow by the gradual inclusion of more rubber, since the crystallized form represents the most stable modification of stretched rubber. Such a process would also be expected to continue to the end of the curve and rupture of the ring, as there seems to be no process which could cause an inflection of the nature of point A . Furthermore, since there are many such crystal "seeds" in one specimen of rubber, the end result of the expansion of such crystal nuclei would be a polycrystalline mass, while curve AB appears to represent essentially a monocrystalline or at least a very regular arrangement. Since forces could hardly be as equally distributed in a polycrystalline mass such a mass would be expected to be the stiffer.

It will be seen that all these effects are in complete agreement with the hysteresis phenomena already discussed.

The Essential Causes of Elasticity

It is of interest to note that since the two parts of the present extension curves must relate to greatly differing molecular arrangements of the rubber chains, but do not differ in the mathematical form of their elastic curves, it is clear, therefore, that the essential nature of elasticity in rubber cannot be assumed to relate to any special molecular arrangement factors, spirals, helices, etc., as has often been attempted.

Arrangement factors as related to the molecular configurations of rubber are in the ultimate analysis simply the interactions of two or more rubber chains on each other, and if such interactions are eliminated as a possible source of elasticity, this would strongly suggest that the basis of elasticity must be related only to the intrinsic properties of single rubber chains, i.e., their kinetic energy, mass, and flexibility.

Kinetic Elasticity of Rubber

In Fig. 6, m is considered as the mass of a portion of the rubber chain, vibrating between two extreme positions at $\pm R$ from the neutral axis; and it is considered that in this vibration, a length $2L$ of chain is taken with it.

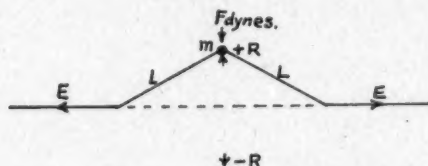


FIG. 6.

The entire chain is, of course, to be considered in the same fashion, and it is therefore taken that the chain is in a uniform elastic tension E , and that it adapts its position to the vibration without change in length.

If the weight is at position r , and f is the force acting on it,

$$f = \frac{2E}{L} r,$$

and it will be seen that m will execute a simple harmonic vibration (with a velocity V at the axis)

$$\therefore \frac{f}{r} = \frac{m V^2}{R^2}.$$

In view of Meyer and Mark's X-ray data (6) on the structure and spacings in rubber the following values are selected as perhaps being possible vibration constants within this structure:

$$\begin{aligned} R &= 2\text{\AA}, \\ L &= 2 \text{ isoprene units or } 8.1 \text{\AA}, \\ m &= 1 \text{ isoprene unit, mol. wt. } 68, \\ V &= \text{gas law velocity of } m \text{ at } 300^\circ \text{ K.} \\ &= 33,200 \text{ cm. per sec.,} \end{aligned}$$

The calculated value of $f/r = 311.8$ dynes per cm. and $E = 1.263 \times 10^{-5}$ dynes per rubber chain.

With a chain spacing of 4.15\AA in one direction and 6.15\AA in the other, this would give a value of $5040 \text{ kgm. per cm.}^2$ for the tension in fully extended crystallized rubber.

Experimentally, rubber gives ultimate tensile strengths up to about $2000 \text{ kgm. per cm.}^2$, based on the actual section when under stress, as in the above calculation, and it is clear therefore that these considerations will in fact provide fully for the required forces of elasticity.

This calculation is, of course, based on mere assumptions of the magnitude of possible vibrations, and it could be repeated for any possible combination of amplitudes and affected chain lengths. For example, the calculation may be applied to individual carbon atoms, although vibration in this case is presumably hindered by the angles of their valence bonds. In this case, an amplitude of 0.5\AA would provide a similar value for the elastic tension of the chain.

It does not appear to be possible to make this calculation on any exact basis, and there are several other factors which would also require consideration:

- (a) The above vibration amplitudes appear to be rather too great; if R is reduced, E increases rapidly.
- (b) Very large tensions calculated in this way will obviously be modified owing to the effect of neighboring atoms. In other words, the mass m "bounces freely" between its neighbors, as well as being partially restrained by tension in the chain.
- (c) The work of elasticity must be added to the gas law kinetic energy of m , if elasticity is explained on a kinetic basis.

The effect of "free bouncing" between neighboring atoms will obviously reduce the tension in the chain concerned, since restriction of vibrations by neighbors and by chain tension will be additive. Furthermore, even in unstretched rubber, there can be no doubt that the same kinetic effects must be fully operative, although no net tension appears in the rubber specimen. Unstretched and stretched rubber may not necessarily utilize the same effective vibrating chain lengths, but there seems no doubt that kinetic processes must be very similar in both. In unstretched rubber, however, the chains are in random attitudes, and no net directional tension is produced, but these kinetic effects would in this case produce an internal pressure in the entire specimen.

It will be seen that the concept that an unstressed piece of rubber experiences a fairly large real internal pressure, of a nondirectional or hydrostatic nature, is not in agreement with usual thought on this matter. For instance, the following is quoted from Alfrey (1), p. 165, para. 2 and 3: "Specifically, a straightened out linear polymer molecule in an unstressed amorphous sample is not under tension in any physical sense. Such a molecule tends to contract, merely because as it carries out its random Brownian movements, it tends to spend equal portions of its time in each equivalent volume of phase space, and most of the volume of phase space corresponds to the contracted state."

If these Brownian movements are to explain the elasticity in *form* of such materials as rubber, there seems no doubt that the correlated *energy* of these movements must also be taken into account, as in the calculation of kinetic elasticity above. The above quoted "straightened out linear molecule" must, therefore, be in a state of real tension, since part of the Brownian movements are at some instants restricted only by the physical presence of the chain. The absorption or deflection of the energy of this Brownian movement must result in a real chain tension of the type already discussed as an idealized vibrating mass m . Furthermore, whether the entire length of a molecule is "straightened out" or not, its component sections must have at all times much the same character; consequently, it must be assumed that all polymer molecules are constantly under tension, even in unstressed specimens.

These chain tensions cannot be considered as "mathematical abstractions" (Alfrey) since there can be no doubt that if a single devious chain passing through a centimeter cube of unstressed rubber could be dissected from the block, it would at once contract to its most probable phase-space relationship, i.e., it would shrink to a sphere or ellipsoid of matter barely, if at all, distinguishable from the initial specimen. Such a contraction is merely the form expression of the kinetic vibratory tension already discussed, and, since all chains are equally tending to contract, the result must be a volumetric, or hydrostatic, pressure. It cannot, of course, be measured by boring a hole into the block and connecting a manometer, but this failure is simply because the instrument is unsuitable.

Rubber has been treated by other workers as an ideal gas, e.g., by Mark (4, 5), but, owing to the lack of examples showing such simple mathematical properties, it has not previously been feasible to illustrate the correctness of this relationship in such a clear manner.

In the present case, however, results are greatly clarified by the fact that the 4th power term gives a real origin to the equations at the point $L = 0$, and, from the previous discussion of rubber extension considered as a sideways compression, if the equations are recalculated as "compressions", it is clear that a "gas" under 13.75 kgm. per cm.² is being considered as under compression.

Young's Modulus

It is interesting to note that the slope of the dotted lines in Fig. 4 is in reality simply the measure of Young's modulus for this fatigued rubber, as expressed in the usual way for other solids.

As ordinarily measured on a solid, Young's modulus represents the stiffness of the section, on the basis of retaining the same number of atoms in that section. In the usual extension test of rubber, however, the number of atoms in the section is reduced almost in direct proportion to the extension, since volume changes are very slight. Consequently, if Young's modulus is to be expressed on the usual basis, the function F/A should be used.

The conclusion, therefore, is reached that with this fatigued rubber, Young's modulus simply represents the internal pressure in the unstretched rubber. With more usual solids, the relation would not be quite as simple since considerable volume changes usually occur on stretching solids; however, if the work of extension by Young's modulus were corrected for the work of the bulk volume change which accompanies it, the same relation might perhaps be of more general application. Even with the fatigued rubber, a small deviation occurs since the slope of F/A at $L = 1$ is already modified very slightly by the initial development of the term in $(L)^4$; in this case, however, the extension curve is subject to analysis and the effect can be evaluated, while similar corrections for other solids would be less readily determined.

S Shape of Elongation Curves

The characteristic shape of the initial part of the elongation curve for rubber is an S shape, and it is of interest to note that the curves of F/A under present discussion show no trace whatever of any residual S shape although the same data presented as the usual $F:L$ curve is of closely the normal form, with a pronounced S shape. It is clear, therefore, that the basic features of the S shape cannot properly be considered as due to two merging curves as discussed by Griffith (2) nor could the inflection point discussed by Shacklock (8) be interpreted as suggesting that elastic phenomena differ below and above this point.

Shacklock reports, however, that a slight residual S shape is present in the first elongation curve of all rubbers, even when calculated as F/A . Since even slight elongation of a new ring does, in fact, result in slight hysteresis and permanent deformation, if the complete elimination of the S shape in F/A curves is a property of the stabilized structure found in fatigued rings, it would be expected as reported by Shacklock that with new rings the S shape could only be approximately eliminated.

Comparison with Previous Data

As far as the author is aware, no similar data on what might be termed "severely stabilized" rubber are presented, but an interesting curve is given by Ornstein, Wouda, and Eymers (7).

The results presented by these authors give a curve of some general similarity to the present, with, however, several major differences: it is not recorded that the rubber was severely fatigued and in fact the results are stated to have been obtained with new rubber; the initial part of their return curve is a straight line; the entire phenomena occur below 380% elongation and the critical or inflection point is at about 250% elongation.

These authors do not discuss the data at much length, but it would appear that their raw rubber differed markedly from the smoked sheet used in present tests, and that, although the rubber may have been "new" in the sense that it was made for the purpose, it would seem probable that their specimens had been stretched a number of times before giving the data recorded, and furthermore, the remarkable singularity of an inflection point in the middle of an elongation curve is not noted.

Most other results with fatigued rubber appear to have been made at high or medium frequencies, and but few records of fatigued stress-strain curves are available. Holt (3), however, gives curves of successive elongations in general very similar to the type here recorded. It is interesting to note, however, that without the severe initial stretching used in the present series, no noticeable inflection points occur in his curves. Superimposition of the curves that he reports for different specimens, however, suggests the same phenomenon which initiated this work, i.e., the curves agree well for lower extensions, but not at higher values.

In connection with the apparent necessity that the forces of elasticity of rubber must be of purely kinetic origin, Griffith (2) has made an interesting attempt to calculate such forces in which it is assumed that lengths of the isoprene chain rotate in the same manner as a "skipping rope", the retraction forces being produced in the essentially inelastic chain by the centrifugal forces involved. The present suggestion is somewhat similar to this, and it should be noted that such a rotation is simply a combination of two simple harmonic vibrations. However, in order that two such vibrations can combine into a rotation, it is necessary that the two vibrations occur at the same place in a chain; that they have essentially the same amplitude and the correct phase relations. It seems an unavoidable conclusion that if such organized vibrations existed at any instant, that the random nature of molecular forces would at once destroy this organization. It is therefore here considered that while the vibrations would persist, they must be considered on a random basis. If, therefore, two such vibrations happened to assume momentarily the proper phase and space relations and could therefore be calculated as rotation, nothing would be added to the analysis by so considering them, as both motions would still be independent and random. It would also seem that while Griffith's calculations are related to an initial stress-strain curve, they should more properly be related to curves for fatigued rubber, since he considers a stabilized elastic structure, while the character of the initial curve

is very greatly affected by the work required to cause permanent modifications in the chain structure which are not contemplated in the mathematical discussion.

Further Extension of Kinetic Elasticity Theories

One of the major difficulties in further attempts to calculate elasticity on a kinetic basis is the major role of the forces between neighboring hydrocarbon chains. These could presumably be considered as gas molecules, but unfortunately, their effective molecular weight and the influence of restrictions at junction points is not known, so the question is still difficult. It would, however, appear necessary to consider vibrations of portions of chains in all directions and chains of all lengths, from one C atom up to the full length between junction points; in all spatial attitudes; and with all random energies round a mean.

Some useful information might perhaps be obtained from the position of the inflection point on the extension curve of fatigued rubber, since, at this point, it is obvious that the gain by redistribution of stress just overbalances the Van der Waal attractions at points where the chains are irregularly entangled, but, without considerably more knowledge of the system, it is not clear what use may be made of this condition.

It would seem, however, that the elasticity of rubber may eventually be calculable from purely kinetic considerations without the need to assume any special spiral or other arrangements of the hydrocarbon chain, or indeed, any special properties of the chain itself except flexibility, a low enough degree of polarity to permit adequate chain freedom, and a suitable degree of cross-linkage.

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